Optical Reflectivity of the Si(111)-(2×1) Surface — The Role of the Electron–Hole Interaction

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We calculate the optical reflectivity of the Si(111)-(2×1) surface from first principles. To this end, we first calculate the quasiparticle band structure of the surface within the *GW* approximation for the electronic self energy. The band structure exhibits two surface bands inside the fundamental bulk band gap. Thereafter the electron–hole interaction is computed for transitions between the relevant bands, the Bethe-Salpeter equation for coupled electron–hole excitations is solved and the optical response is evaluated. In the energy range below the fundamental bulk band gap, the reflectivity spectrum is dominated by a surface exciton at 0.43 eV with an excitonic binding energy of 0.26 eV. Our calculated spectrum is in very good agreement with experimental data from differential reflectivity spectroscopy.

1. Introduction

The role of electron–hole interaction and excitonic effects on the optical properties of surfaces has been an issue of discussion for a long time [1 to 8]. For some systems, the surface effects on optical spectra arise mainly from the electronic band structure of the surface, i.e. the spectrum can be described by interband vertical electron–hole excitations between hole and electron states, and correlation effects due to electron–hole interaction are not very important. In other systems, however, spectral features have been identified that arise from coupled electron–hole excitations, such as surface excitons. This holds in particular for surfaces that exhibit occupied and empty surface bands inside the fundamental bulk band gap. In such systems, electron–hole pairs can be excited that are localized at the surface, with excitation energies way below the bulk band-gap energy. For such localized states, the electron–hole interaction is strongly enhanced as compared to the bulk, and significant excitonic effects show up in the optical spectrum. One prototype system in which such effects are very important is the Si(111)-(2×1) surface [7, 8]. In the present paper we calculate the reflectivity of this surface from first principles.

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2. Theoretical Approach

Optical excitations are two-particle processes, involving simultaneous creation of electrons and holes. This is described by the two-particle Green's function of the electronic system [9]. Its calculation requires information about the single-particle Green's function, as well as, about the electronic ground state. Therefore, one has to follow a hierarchy of three different *ab-initio* techniques. In the first step, we perform an LDA calculation of the surface system to obtain its geometric structure and the electronic ground-state configuration. Thereafter, we calculate the quasiparticle (QP) band structure of the surface (i.e., the spectrum of the single-particle Green's function) within the *GW* approximation for the electron self-energy operator [10]. In the third and final step, we evaluate the electron–hole interaction between the relevant bands and solve the Bethe-Salpeter equation for the two-particle Green's function [11 to 13]. This approach yields the coupled electron–hole excitations of the surface system, in particular the surface excitons. From those, we can evaluate the optical response of the surface including all surface effects.

The first two steps, i.e. the LDA and the *GW* calculations, are standard techniques that have been successfully applied to a large variety of different systems [10]. In the present situation, we use a supercell geometry with eight layers of Si and a vacuum layer of 8 Å. One of the two slab surfaces is terminated by hydrogen atoms. We employ norm-conserving ab-initio pseudopotentials. Both for the wavefunctions, as well as for the two-point functions occurring in the *GW* calculation, localized Gaussian orbitals are used as basis functions [14]. In the *GW* calculation, the static dielectric function is calculated within the random-phase approximation (RPA) and is then extended to finite frequencies in a generalized plasmon-pole model.

Based on the results of a QP band-structure calculation, one can now investigate coupled electron–hole excitations. They are expressed as

$$|S\rangle = \sum_{\mathbf{k}} \sum_{\mathrm{v}}^{\mathrm{hole}} \sum_{\mathrm{c}}^{\mathrm{elec}} A_{\mathrm{vc}\mathbf{k}}^{S} \hat{a}_{\mathrm{v}\mathbf{k}}^{\dagger} \hat{b}_{\mathrm{c}\mathbf{k}}^{\dagger} |0\rangle \,, \tag{1}$$

where $\hat{a}_{\mathrm{v}\mathbf{k}}^{\dagger}$ and $\hat{b}_{\mathrm{c}\mathbf{k}}^{\dagger}$ create a quasi-hole in the valence band v and a quasi-electron in the conduction band c, respectively. The wave vectors $\mathbf{k}$ are from an appropriate mesh in the Brillouin zone (see below). The excitation energies Ω_S and the coefficients $A_{\mathrm{vc}\mathbf{k}}^{S}$ of the excitations $|S\rangle$ can be evaluated from the Bethe-Salpeter equation [9]

$$(\varepsilon_{\mathrm{c}\mathbf{k}}^{\mathrm{QP}} - \varepsilon_{\mathrm{v}\mathbf{k}}^{\mathrm{QP}}) A_{\mathrm{vc}\mathbf{k}}^{S} + \sum_{\mathrm{v}'\mathrm{c}'\mathbf{k}'} \langle \mathrm{vc}\mathbf{k}| K^{\mathrm{eh}} |\mathrm{v}'\mathrm{c}'\mathbf{k}\rangle A_{\mathrm{v}'\mathrm{c}'\mathbf{k}'}^{S} = \Omega_S A_{\mathrm{vc}\mathbf{k}}^{S} \,. \tag{2}$$

The energies $\varepsilon_{m\mathbf{k}}^{\mathrm{QP}}$ are the QP band-structure energies from the preceding *GW* calculation. The key quantity in Eq. (2) is the electron–hole interaction $\langle \mathrm{vc}\mathbf{k}| K^{\mathrm{eh}} |\mathrm{v}'\mathrm{c}'\mathbf{k}\rangle$ which is responsible for the coupling of the interband transitions ($\mathrm{v}\mathbf{k} \rightarrow \mathrm{c}\mathbf{k}$) to one another. In particular, the interaction gives rise to coupling of transitions at different $\mathbf{k}$-points, thus leading to spatial correlation of electrons and holes in the excited state. For the optically excitable spin-singlet transitions, the matrix elements of the electron–hole interaction are calculated as six-dimensional real-space integrals

$$\langle \mathrm{vc}\mathbf{k}| K^{\mathrm{eh}} |\mathrm{v}'\mathrm{c}'\mathbf{k}'\rangle = - \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \, \psi_{\mathrm{c}\mathbf{k}}^{*}(\mathbf{r}) \, \psi_{\mathrm{c}'\mathbf{k}'}(\mathbf{r}) \, W(\mathbf{r}, \mathbf{r}') \, \psi_{\mathrm{v}\mathbf{k}}(\mathbf{r}') \, \psi_{\mathrm{v}'\mathbf{k}'}^{*}(\mathbf{r}')$$
$$+ 2 \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \, \psi_{\mathrm{c}\mathbf{k}}^{*}(\mathbf{r}) \, \psi_{\mathrm{v}\mathbf{k}}(\mathbf{r}) \, v(\mathbf{r}, \mathbf{r}') \, \psi_{\mathrm{c}'\mathbf{k}'}(\mathbf{r}') \, \psi_{\mathrm{v}'\mathbf{k}'}^{*}(\mathbf{r}') \,. \tag{3}$$

The first term is an attractive direct interaction term while the second term describes the repulsive exchange interaction. $\psi_{m\mathbf{k}}(\mathbf{r})$ are the quasiparticle wavefunctions of electrons and holes, respectively. $v(\mathbf{r}, \mathbf{r}') = e^2/|\mathbf{r} - \mathbf{r}'|$ is the bare Coulomb interaction and $W(\mathbf{r}, \mathbf{r}')$ is the screened Coulomb interaction which we calculate within RPA.

After solving Eq. (2) we evaluate the optical spectrum, in particular the differential reflectivity spectrum $\Delta R/R(\omega)$. For the energy range below the bulk band gap, it is given by [4]

$$\frac{\Delta R}{R}(\omega) = 4\frac{\omega}{c}\frac{\mathrm{Im}\left(d\epsilon^{\mathrm{surf}}(\omega)\right)}{\epsilon_{\mathrm{b}} - 1} \qquad (4)$$

with ϵ_{b} being the bulk dielectric constant and d the surface thickness. The dielectric response $\mathrm{Im}\left(d\epsilon^{\mathrm{surf}}(\omega)\right)$ of the surface results from the solutions of the Bethe-Salpeter equation (2), including the corresponding optical transition matrix elements.

3. Results and Discussion

The structure of the surface is shown in Fig. 1 as a side view. The surface is terminated by π-bonded chains of Si atoms along the [01$\bar{1}$] direction, as discussed by Pandey [15]. We find that the chain is buckled with a height difference of 0.51 Å between the up and down atoms. The surface atoms are bonded by only three bonds instead of the usual four sp^3 bonds. The remaining p_z-like dangling-bond orbitals are coupled along the chain and form π-like states. In the band structure, they give rise to two surface bands, D_{up} and D_{down}, inside the fundamental bulk band gap (see Fig. 2). The occupied D_{up} band is formed from the dangling-bond orbitals at the surface atoms which are relaxed outwards (up atoms). The unoccupied D_{down} band, on the other hand, consists of the orbitals at the surface atoms which are relaxed towards the crystal (down atoms). Between the two bands, there is a direct surface band gap of 0.69 eV along the JK high-symmetry line. Our calculated band-structure energies are in excellent agreement with a previous GW calculation [7] and with experimental data from direct and inverse photoemission spectroscopy [16] (included in Fig. 2 as dots).

From the electronic structure of the surface one can expect that excitonic effects are very strong. On the one hand, the electron–hole interaction is stronger at surfaces than in the bulk, in general, due to the reduced dielectric screening at the surface and its two-dimensional character. In addition, the surface states of the present system are nearly fully decoupled from the bulk crystal. Their bands are inside the bulk band gap, and the electron and hole states are strongly localized on the surface chains. Therefore,
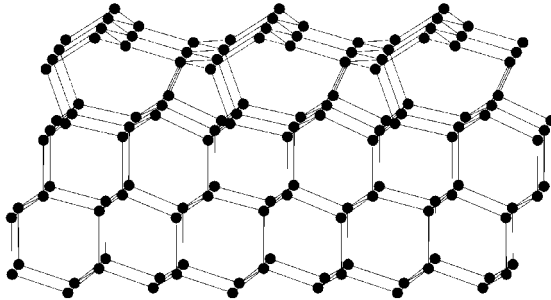

Fig. 1. Structure of the Si(111)-(2×1) surface (side view). The Pandey chains run along the [01$\bar{1}$] direction perpendicular to the drawing plane
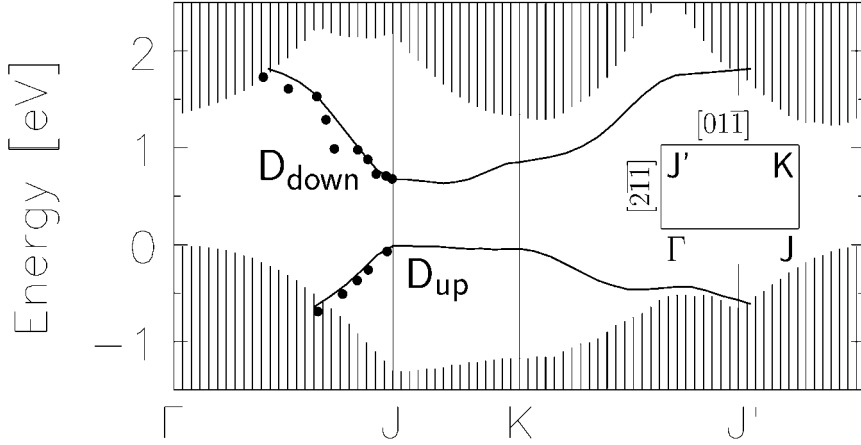
Fig. 2. *GW* quasiparticle band structure of the Si(111)-(2×1) surface. The shaded areas denote Si bulk states. The dots denote experimental data [16]

the spatial overlap between the electron and hole wavefunctions is much larger than in bulk semiconductors, thus further increasing the electron–hole interaction.

In order to describe the correlated electron–hole pair states and surface excitons, one has to numerically evaluate the Bethe-Salpeter equation (2) on an appropriate mesh of **k**-points. In particular, the dispersion of the band structure has to be taken into account. In the present case, the anisotropy in the surface band dispersion requires an anisotropic mesh. In the direction perpendicular to the Pandey chains, i.e. along the JK high-symmetry line, a mesh density of ten **k**-points ($\Delta k_x \approx 0.05$ at. units) is sufficient due to the weak dispersion of the surface bands. In the direction along the chains (along the ΓJ high-symmetry line), on the other hand, a much higher density of about 100 points ($\Delta k_y \approx 0.01$ at. units) is necessary to account for the strong dispersion of the surface bands. We are, however, mainly interested in the low-energy excitations below the bulk band-gap energy. These excitations are mainly formed from electron–hole pair configurations $|vc\mathbf{k}\rangle$ with **k** being close to the JK line (where the surface band gap has its minimum). Therefore the mesh can be restricted to points in the vicinity of the JK high-symmetry line. Further away from the JK line, the gap between the two surface bands becomes so large that transitions $|vc\mathbf{k}\rangle$ between them do not contribute to the lowest-energy surface excitons and can be excluded from the BSE.

The calculated differential reflectivity spectrum is shown in Fig. 3. The solid curve results from Eq. (2), i.e. excitonic correlation effects due to the electron–hole interaction are included. The dashed curve, on the other hand, was calculated from vertical transitions between the surface bands, i.e. excitonic effects are neglected. Without the interaction, the onset of the spectrum is at the direct surface band gap of 0.69 eV. When the electron–hole interaction is included, the spectrum is completely changed. Above the surface band gap, the excitations observe a strongly destructive superposition of oscillator strength and the amplitude of the spectrum is reduced by one order of magnitude. Below the surface band gap, on the other hand, a number of surface excitons show up, forming a discrete spectrum. The lowest of these excitons, at an energy of 0.43 eV, has a large dipole matrix element (due to constructive superposition of the
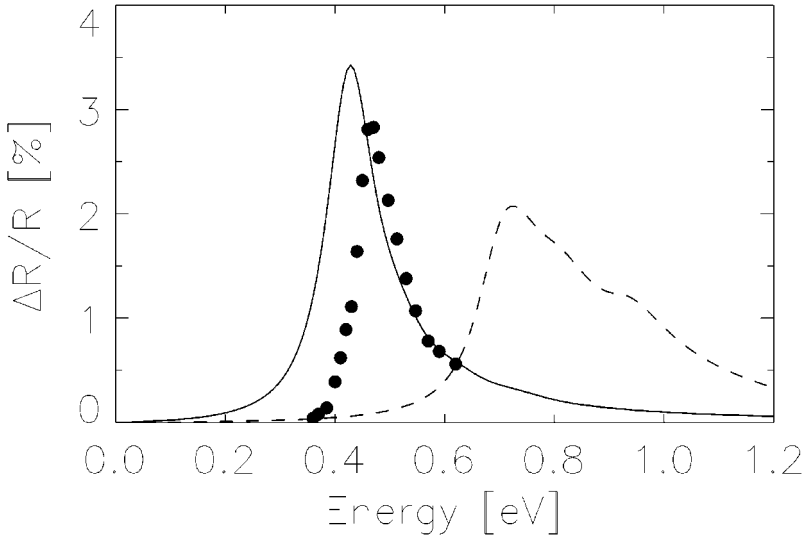
Fig. 3. Differential reflectivity spectrum of the Si(111)-(2×1) surface, calculated for normal incidence. The solid (dashed) curves include (neglect) electron–hole interaction. An artificial broadening of 0.05 eV is included. The dots denote experimental data by Ciccacci et al. [2]

contributing optical transition matrix elements) and dominates the reflectivity spectrum. The other surface excitons at higher energies have much smaller optical strength and do not contribute strongly to the spectrum. They only give rise to the slightly higher right-hand portion of the main peak.

The differential reflectivity of the Si(111)-(2×1) surface has been measured by Chiaradia et al. [1] and by Ciccacci et al. [2]. We include the data by Ciccacci et al. in Fig. 3. They show a single peak at 0.47 eV due to the lowest-energy surface exciton. Both our calculated excitation energy (0.43 eV) and our calculated absorption strength are in good agreement with the measured data, thus confirming that we have included all relevant physical aspects in our first-principles approach.

Due to the strong electron–hole interaction, the excitonic effects are enormous. The excitonic binding energy of the lowest-energy exciton amounts to 0.26 eV, i.e. it is 15 times larger than the binding energy of bulk Si (15 meV). Our calculated binding energy is larger than the value of 0.13 eV obtained in a previous model calculation by Northrup et al. [7] and slightly smaller than the model result of 0.3 eV by Reining and Del Sole [8]. As discussed above, the increased binding energy results from the localized character of the contributing surface states that are nearly completely decoupled from the bulk crystal. Concomitantly, the surface excitons consist to more than 99% of transitions between D_{up} and D_{down}. The contributions of other transitions, involving bulk states, are nearly negligible.

4. Conclusions

In summary, we have calculated the optical reflectivity of the Si(111)-(2×1) surface within an *ab-initio* approach. To this end, we computed the quasiparticle band structure of the surface which shows two surface bands inside the fundamental bulk band gap.

Based on this, we have calculated the electron–hole interaction for transitions between the relevant bands, and we have solved the Bethe-Salpeter equation for coupled electron–hole excitations. We find a number of bound surface excitons below the surface band gap, with excitonic binding energies that are much larger than the ones in bulk Si. The resulting optical spectrum of the surface is in very good agreement with experimental data. This demonstrates the importance of excitonic effects in the optical excitation spectrum of semiconductor surfaces, in particular for surfaces which exhibit dangling-bond states with energies inside the bulk band gap.

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